

Amendment, Applicants have adopted the Examiner's suggestion and have corrected the non-conventional English spelling by replacing "hydrogenfluoride" with "hydrogen fluoride" thereby obviating the rejection to claims 5-8.

In addition, claims 4-5, 9 and 10 were rejected for reciting the term "organic solvent having a hetero atom". By this Amendment, Applicants have amended claims 4-5, 9 and 10 to now recite "an organic solvent comprising molecules having a hetero atom" to more clearly and succinctly recite Applicants' invention. Subject matter basis for this Amendment can be found in the specification as filed on page 7, line 14 to page 8, line 24. Further, Applicants submit that one of ordinary skill in the art would readily appreciate that the conventional term in the art, "hetero atom", refers to an odd or dissimilar atom in the ring of a heterocyclic compound (see **Attachment C** – definition of "hetero atom"). Therefore, Applicants respectfully submit that claims 4-5, 9 and 10 as amended are not indefinite and therefore respectfully request that the rejection to these claims under 35 U.S.C. § 112, second paragraph, be withdrawn.

Claims 1-4, 9, and 14-15 were rejected under 35 U.S.C. § 103(a) as being unpatentable over Wojtczak et al US Pat. No. 6,280,651 (hereinafter "Wojtczak"). Applicants respectfully submit that Wojtczak is not prior art of the present application under 35 U.S.C. § 103(a). The present application has a priority date of November 24, 1998 corresponding to the priority Japanese Patent Application No. 1998-332767. Enclosed with this Amendment, Applicants have provided an English translation of that priority document. Wojtczak has a filing date of December 16, 1998 and an issue date of August 28, 2001. Therefore, Wojtczak is not prior art of the present application under

35 U.S.C. § 103(a). Therefore, Applicants respectfully request that the Examiner withdraw the rejection to claims 1-4, 9, and 14-15 as being unpatentable over Wojtczak.

Claims 1-5, 9-10 and 14-15 were rejected under 35 U.S.C. § 103(a) as being unpatentable over Bowden et al US Pat. No. 5,320,709 (hereinafter "Bowden"). The Examiner asserts that Bowden discloses a process for wet etching a BPSG layer and a thermal SiO₂ layer using a solution comprised of 4% NH₄F, 96% polyhydric alcohol at a temperature of 20-40°C. Further, the Examiner asserts that the etch rate of the BPSG is 4 angstroms at 25°C and an etch rate of the thermal SiO₂ of 14 angstroms at 25°C (the Examiner citing Bowden, columns 2-4 and Figures 2-4).

The claimed invention is directed to an etching solution having a thermal oxide (THOX) film etch rate and boron phosphosilicate glass (BPSG) film etch rate at 25°C of 100 angstroms/mn or lower and a ratio of (BPSG etch rate)/(THOX etch rate) of 1.5 or lower.

Contrary to the Examiner's assertion, Bowden clearly fails to teach or suggest the claimed ratio of (BPSG etch rate) [divided by] (THOX etch rate) and therefore Bowden fails to make the claimed invention obvious. Contrary to the Examiner's assertion, Figure 2 in Bowden clearly discloses the etch rate of BPSG is 14 angstroms at 25°C, not 4 angstroms as alleged by the Examiner. Further, Figure 2 clearly shows the etch rate of the thermal SiO₂ is 4 angstroms at 25°C not 14. Using the clearly disclosed BPSG etch rate of 14 angstroms, the ratio of the (BPSG etch rate)/(THOX etch rate) at 25°C in Figure 2 is 3.5. In sharp contrast to that of Bowden, the claimed invention clearly recites a (BPSG etch rate)/(THOX etch rate) of 1.5 or lower.

Therefore, Bowden's ratio of 3.5 is outside of the scope of the claimed invention and consequently, Bowden fails to teach or suggest the claimed invention.

Moreover, in sharp contrast to the clear teaching of Bowden, the present invention enables THOX and BPSG to be etched at nearly the same rate (see page 10, lines 21-25 of the present specification). On the contrary, Bowden clearly teaches different etch rates and thus teaches away from nearly the same rates.

Based on the foregoing discussion, Applicants respectfully submit that claims 1-5, 9-10 and 14-15 are not made obvious by Bowden and therefore respectfully request that the rejection under 35 U.S.C. § 103(a) to these claims be withdrawn.

Applicants gratefully appreciate the Examiner's indication of allowable subject matter of claims 6-8 and 11-13. By this Amendment, Applicants submit that all prior rejections are overcome, and that all pending claims are now in condition for allowance.

In view of the foregoing, Applicants respectfully submit that the present application is in condition for immediate allowance, and such action is earnestly solicited.

Respectfully submitted,

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November 14, 2002


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ATTACHMENT A

Marked Up Replacement Claims

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Following herewith is a marked up copy of each rewritten claim.

4. (Amended) The etching solution according to claim 1 comprising at least one member selected from the group consisting of an organic acid and an organic solvent comprising molecules having a hetero atom.

5. (Amended) The etching solution according to claim 1 comprising (i) ammonium hydrogen fluoride, (ii) water and (iii) at least one member selected from the group consisting of an organic acid and an organic solvent comprising molecules having a hetero atom, the water being contained in a concentration of 3% by weight or lower.

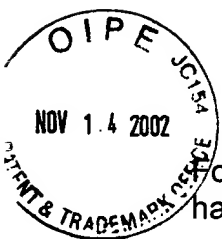
6. (Amended) The etching solution according to claim 1 comprising ammonium hydrogen fluoride, water and isopropyl alcohol, the water being contained in a concentration of 3% by weight or lower.

7. (Amended) The etching solution according to claim 1 comprising ammonium hydrogen fluoride, water and ethanol, the water being contained in a concentration of 3% by weight or lower.

8. (Amended) The etching solution according to claim 1 comprising ammonium hydrogen fluoride, water and acetone, the water being contained in a concentration of 3% by weight or lower.

9. (Amended) The etching solution according to claim 1 comprising (i) ammonium fluoride and (ii) at least one member selected from the group consisting of an organic acid and an organic solvent comprising molecules having a hetero atom.

10. (Amended) The etching solution according to claim 1 comprising (i) ammonium fluoride, (ii) water and (iii) at least one member selected from the group consisting of an organic acid and an organic solvent comprising molecules having a hetero atom, the water being contained in a concentration of 10% by weight or lower.



ATTACHMENT B

Clean Replacement Claims

Following herewith is a clean copy of each claim which replaces each previous claim having the same number.

4. (Amended) The etching solution according to claim 1 comprising at least one member selected from the group consisting of an organic acid and an organic solvent comprising molecules having a hetero atom.

A. 5. (Amended) The etching solution according to claim 1 comprising (i) ammonium hydrogen fluoride, (ii) water and (iii) at least one member selected from the group consisting of an organic acid and an organic solvent comprising molecules having a hetero atom, the water being contained in a concentration of 3% by weight or lower.

6. (Amended) The etching solution according to claim 1 comprising ammonium hydrogen fluoride, water and isopropyl alcohol, the water being contained in a concentration of 3% by weight or lower.

7. (Amended) The etching solution according to claim 1 comprising ammonium hydrogen fluoride, water and ethanol, the water being contained in a concentration of 3% by weight or lower.

8. (Amended) The etching solution according to claim 1 comprising ammonium hydrogen fluoride, water and acetone, the water being contained in a concentration of 3% by weight or lower.

9. (Amended) The etching solution according to claim 1 comprising (i) ammonium fluoride and (ii) at least one member selected from the group consisting of an organic acid and an organic solvent comprising molecules having a hetero atom.

A¹
cont

10. (Amended) The etching solution according to claim 1 comprising (i) ammonium fluoride, (ii) water and (iii) at least one member selected from the group consisting of an organic acid and an organic solvent comprising molecules having a hetero atom, the water being contained in a concentration of 10% by weight or lower.

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hetero atom

An odd atom in the ring of a heterocyclic compound. For instance, nitrogen is the hetero atom in pyridine.

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ATTACHMENT C

VERIFICATION OF TRANSLATION

Re: JAPANESE PATENT APPLICATION NO. 1998-332767

I, Ikuko AIHARA, of Kitahama TNK Building,
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hereby declare that I am the translator of the
document attached and certify that the following is
true translation to the best of my knowledge and
belief.

Signature of translator Ikuko Aihara
Ikuko AIHARA

Dated this 31st day of October, 2002



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[Document Name] Specification

[Title of the Invention] Etching solution

[Claims]

[Claim 1]

5 An etching solution having a thermal oxide (THOX) film etch rate and boron phosphosilicate glass (BPSG) film etch rate at 25°C of 100Å/min or lower and a ratio of (BPSG etch rate) / (THOX etch rate) of 1.5 or lower.

10 [Claim 2]

 The etching solution according to claim 1 comprising at least one member selected from the group consisting of fluoride salts and bifluoride salts.

[Claim 3]

15 The etching solution according to claim 2, wherein the solvent of the etching solution has a relative dielectric constant of 35 or lower.

[Claim 4]

20 The etching solution according to claim 2 or claim 3 comprising at least one member selected from the group consisting of organic acids and organic solvents having hetero atom(s).

[Claim 5]

25 The etching solution according to claim 1 comprising ammonium hydrogenfluoride and water, and at least one member selected from the group consisting of

organic acids and organic solvents having hetero atoms,
wherein the content of water is 3% by weight or lower.

[Claim 6]

The etching solution according to claim 1
5 comprising ammonium hydrogenfluoride, water and isopropyl
alcohol, wherein the concentration of water is 3% by
weight or lower.

[Claim 7]

The etching solution according to claim 1
10 comprising ammonium hydrogenfluoride, water, and ethanol,
wherein the concentration of water is 3% by weight or
lower.

[Claim 8]

The etching solution according to claim 1
15 comprising ammonium hydrogenfluoride, water and acetone,
wherein the concentration of water is 3% by weight or
lower.

[Claim 9]

The etching solution according to claim 1
20 comprising ammonium fluoride and at least one member
selected from the group consisting of organic acids and
organic solvents having hetero atom(s).

[Claim 10]

The etching solution according to claim 1
25 comprising ammonium fluoride, water, and at least one
member selected from the group consisting of organic acids

and organic solvents having hetero atoms, wherein the concentration of water is 10% by weight or lower.

[Claim 11]

The etching solution according to claim 1
5 comprising ammonium fluoride, water and ethanol, wherein the concentration of water is 10% by weight or lower.

[Claim 12]

The etching solution according to claim 1
comprising ammonium fluoride, water and isopropyl alcohol,
10 wherein the concentration of water is 10% by weight or lower.

[Claim 13]

The etching solution according to claim 1
comprising ammonium fluoride, water and acetic acid,
15 wherein the concentration of water is 1.5% by weight or lower.

[Claim 14]

A method for producing an etched article by
etching an article with the etching solution as defined in
20 any of claims 1-13.

[Claim 15]

An etched article which is produced by the
method of claim 14.

25 [Detailed Description of the Invention]

[0001]

[Technical Field to Which the Invention Pertains]

The present invention relates to an etching solution, a method for producing an etched article and an etched article produced by the method, more specifically, to an etching solution etching doped oxide films such as boron phosphosilicate glass (BPSG) film and undoped oxide films such as thermal oxide (THOX) film at the same etch rate or similar etch rate, a method for producing an etched article, and an etched article produced by the method.

[0002]

[Prior Art and Problem to be Solved by the Invention]

Conventionally, as etchants for silicon wafers and the like, buffered hydrofluoric acids have been used which comprise HF (50-wt.% aqueous solution) and NH_4F (40-wt.% aqueous solution) mixed in a ratio capable of achieving a desired etch rate.

[0003]

However, the buffered hydrofluoric acids etch doped oxide films such as BSG (boron silicate glass film), BPSG, PSG (phosphosilicate glass film), AsSg (phosphosilicate glass film) and the like faster than they etch undoped oxide films such as TEOS (oxide film formed by CVD method using tetraethoxysilane gas) and like USG, THOX and the like. Therefore, the buffered hydrofluoric acids can not etch the doped oxide films and

undoped oxide films at the same rate.

[0004]

An object of the present invention is to provide an etching solution and an etching method for
5 etching undoped oxide films such as TEOS, THOX and the like and oxide films doped with impurities at the same rate.

[0005]

[Means for Solving the Problem]

10 The present invention relates to the items 1-15 listed below.

Item 1. An etching solution having a thermal oxide (THOX) film etch rate and boron phosphosilicate glass (BPSG) film etch rate at 25°C of 100Å/min or lower and a ratio of
15 (BPSG etch rate) / (THOX etch rate) of 1.5 or lower.

Item 2. The etching solution according to item 1 comprising at least one member selected from the group consisting of fluoride salts and bifluoride salts.

Item 3. The etching solution according to item 2, wherein
20 the solvent of the etching solution has a relative dielectric constant of 35 or lower.

Item 4. The etching solution according to item 2 or 3 comprising at least one member selected from the group consisting of organic acids and organic solvents having
25 hetero atoms.

Item 5. The etching solution according to item 1

comprising ammonium hydrogenfluoride and water, further comprising at least one member selected from the group consisting of organic acids and organic solvents having hetero atoms, wherein the concentration of water is 3% by weight or lower.

Item 6. The etching solution according to item 1 comprising ammonium hydrogenfluoride, water and isopropyl alcohol, wherein the concentration of water is 3% by weight or lower.

Item 7. The etching solution according to item 1 comprising ammonium hydrogenfluoride, water and ethanol, wherein the concentration of water is 3% by weight or lower.

Item 8. The etching solution according to item 1 comprising ammonium hydrogenfluoride, water and acetone, wherein the concentration of water is 3% by weight or lower.

Item 9. The etching solution according to item 1 comprising ammonium fluoride and at least one member selected from the group consisting of organic acids and organic solvents having hetero atom(s).

Item 10. The etching solution according to item 1 comprising ammonium fluoride, water and further comprising at least one member selected from the group consisting of organic acids and organic solvents having hetero atoms, wherein the concentration of water is 10% by weight or

lower.

Item 11. The etching solution according to item 1 comprising ammonium fluoride, water and ethanol, wherein the concentration of water is 10% by weight or lower.

5 Item 12. The etching solution according to item 1 comprising ammonium fluoride, water and isopropyl alcohol, wherein the concentration of water is 10% by weight or lower.

Item 13. The etching solution according to item 1
10 comprising ammonium fluoride, water and acetic acids, wherein the concentration of water is 1.5% by weight or lower.

Item 14. A method for producing an etched article by etching an article with the etching solution as defined in
15 any of items 1-13.

Item 15. An etched article which is produced by the method of item 14.

[0006]

[Mode for Carrying out the Invention]

20 The etching solution of the present invention has the ratio of BPSG etch rate / THOX etch rate at 25°C of 1.5 or lower, preferably 1.3 or lower, more preferably 1.2 or lower, still more preferably 1.1 or lower, particularly 1.05 or lower.

25 [0007]

The BPSG is used for measuring etch rate after

being formed as a film and annealed.

[0008]

The etching solution of the present invention satisfies the above ratio of the etch rates, and also has
5 a THOX etch rate and a BPSG etch rate at 25°C of 100Å/min or lower, preferably 80Å/min or lower, still more preferably 60Å/min or lower, particularly 50Å/min or lower.

[0009]

10 The etch rate of the etching solution of the invention can be determined by etching BPSG and THOX with the etching solution at 25°C and dividing the difference in the film thickness before and after being etched by the etch time.

15 [0010]

Examples the fluoride salts and bifluoride salts of the present invention include metal salts, ammonium salts and quaternary ammonium salts. Preferable examples of the metal salts include those which have high
20 solubility, such as potassium fluoride, sodium fluoride, potassium hydrogenfluoride, sodium hydrogenfluoride and the like. Examples of the ammonium salts include ammonium fluoride and ammonium hydrogenfluoride (ammonium monohydrogendifluoride). Examples of the quaternary
25 ammonium salts include tetramethylammonium fluoride, methylamine hydrofluoride, 2-hydroxyethyltrimethyl-

ammonium fluoride, tetramethylammonium hydrogenfluoride and the like.

[0011]

In the present invention, the relative
5 dielectric constant is that of the solvent (an organic solvent having hetero atom(s), an organic acid or water) measured at 25° C.

[0012]

The relative dielectric constant is usually 35
10 or lower, preferably 25 or lower, more preferably 21 or lower.

[0013]

Ammonium monohydrogendifluoride to be used in the etching solution of the invention may be in the form
15 of crystals or an aqueous solution. Alternatively, stoichiometric amounts of ammonium fluoride and HF may be added to the solvent to form ammonium hydrogenfluoride in the solution.

[0014]

20 The ammonium fluoride to be used in the etching solution of the invention may be in the form of crystals or an aqueous solution.

[0015]

Examples of the organic acids include acetic
25 acid, propionic acid, butyric acid, isobutyric acid, valeric acid, caproic acid, caprylic acid,

monochloroacetic acid, dichloroacetic acid,
trichloroacetic acid, monofluoroacetic acid,
difluoroacetic acid, trifluoroacetic acid, α -
chlorobutyric acid, β -chlorobutyric acid, γ -chlorobutyric
5 acid, lactic acid, glycolic acid, pyruvic acid, glyoxalic
acid, acrylic acid and like monocarboxylic acids,
methanesulfonic acid, toluenesulfonic acid and like
sulfonic acids, oxalic acid, succinic acid, adipic acid,
tartaric acid, citric acid and like polycarboxylic acids.

10 [0016]

Examples of the organic solvents having hetero
atoms include methanol, ethanol, isopropyl alcohol (IPA),
1-propanol, 1-butanol, 2-butanol, t-butanol, 2-methyl-1-
propanol, 1-pentanol, 1-hexanol, 1-heptanol, 4-heptanol,
15 1-octanol, 1-nonyl alcohol, 1-decanol, 1-dodecanol and
like alcohols; ethylene glycol, 1,2-propanediol,
propylene glycol, 2,3-butanediol, glycerin and like
polyols, acetone, acetylacetone, methyl ethyl ketone and
like ketones; acetonitrile, propionitrile, butyronitrile,
20 isobutyronitrile, benzonitrile and like nitriles;
formaldehyde, acetaldehyde, propionaldehyde and like
aldehydes; ethylene glycol monomethyl ether, ethylene
glycol monoethyl ether and like alkylene glycol
monoalkyl ethers; tetrahydrofuran, dioxane and like
25 ethers, trifluoroethanol, pentafluoropropanol, 2,2,3,3-
tetrafluoropropanol and like fluorinated alcohols,

sulfolane, nitromethane and the like.

[0017]

The content of ammonium monohydrogendifluoride is about 0.01-5% by weight, preferably about 0.01-2.5% by weight.

[0018]

The content of ammonium fluoride is preferably about 0.01-4% by weight, more preferably about 0.01-2% by weight.

10 [0019]

The water content is preferably 10% by weight or lower, more preferably about 3% by weight or lower.

[0020]

The content of the organic acid is preferably 15 95% by weight or higher, more preferably 96% by weight or higher.

[0021]

The content of the organic solvent having hetero atom(s) is preferably 85% by weight or higher, 20 more preferably 95% by weight or higher.

[0022]

Preferable etching solutions of the present invention and their compositions are shown below.

- Ammonium monohydrogendifluoride : IPA : water = 0.01-5%
25 by weight : 92-99.99% by weight : 0-3% by weight;
- Ammonium monohydrogendifluoride : ethanol : water =

0.01-5% by weight : 92-99.99% by weight : 0-3% by weight;

- Ammonium monohydrogendifluoride : acetone : water =

0.01-5% by weight : 92-99.99% by weight : 0-3% by weight;

- Ammonium fluoride : IPA : water = 0.01-4% by weight :

5 86-99.99% by weight : 0-10% by weight;

- Ammonium fluoride : acetic acid : water = 0.01-4% by weight : 94.5-99.99% by weight : 0-1.5% by weight;

- Ammonium fluoride : ethanol : water = 0.01-5% by weight : 86-99.99% by weight : 0-10% by weight.

10 [0023]

The etching solution of the invention can be suitably used for etching articles having oxide films doped with B, P, As and the like (BSG, BPSG, PSG, AsSG, etc.) and an undoped oxide films including USG such as

15 THOX, TEOS and the like.

[0024]

In the etching method of the present invention, the temperature of the etching solution is about 15-40°C, and the etch time is about 0.25-10 minutes.

20 [0025]

Examples of the articles to be etched are single crystalline silicon wafers, gallium-arsenic wafers and like wafers, preferably articles comprising a doped oxide film (BSG, BPSG, PSG, AsSG, etc.) and an undoped

25 oxide film (THOX, TEOS and like USG).

[0026]

[Effect of the Invention]

The present invention provides an etching solution and a method for producing an etched article capable of etching THOX, TEOS and like USG and an oxide
5 film doped with impurities, such as BPSG, BSG and the like at nearly the same rate, and an etched article produced by the method.

[0027]

[Examples]

10 The present invention will be explained in more detail referring to Examples and Comparative Examples given below.

[0028]

Hereinafter, the relative dielectric constant
15 is that of the solvent (an organic solvent having a hetero atom, an organic acid or water) at 25°C.

[0029]

The etch rate was determined by measuring the thickness of the films before and after the etching using
20 Auto EL-III ellipsometer manufactured by Rudolf Research.

[0030]

The etch rate of the etching solution was calculated by etching each film with the etching solution at 25°C and dividing the difference in the film thickness
25 before and after being etched by the etch time.

Examples 1-3 and Comparative Examples 1-2

Ammonium monohydrogendifluoride ($\text{NH}_4\text{F}\cdot\text{HF}$),
water and an organic solvent having a hetero atom were
mixed at the ratios shown in Table 1. The mixtures were
5 filtrated using a filter paper to remove crystals
therefrom, giving etching solutions. The etch rate and
etch selectivity of the etching solutions were determined
using two test substrates: one comprising a silicon
substrate and a THOX film formed thereon, the other
10 comprising a silicon substrate and a BPSG film formed
thereon.

[0031]

The results are shown in Table 1.

[0032]

Table 1

Ammonium monohydrogendifluoride/organic solvent/water etching solution

	Organic solvent	Relative dielectric constant	NH ₄ F·HF concentration (%)	Organic solvent concentration (%)	Water concentration (%)	THOX etch rate (Å/min.)	BPSG etch rate (Å/ml n.)	Selectivity
Ex. 1	IPA	19.9	2.28	96.22	1.5	58	52	0.90
Ex. 2	Acetone	20.7	2.28	96.22	1.5	16	18	1.13
Ex. 3	Ethanol	24.6	2.28	96.22	1.5	31	37	1.19
Comp. Ex. 1	Ethanol	32.7	2.28	96.22	1.5	63	120	1.90
Comp. Ex. 2	(Water)	78.3	2.28	0	97.72	44	358	8.14

Examples 4-7 and Comparative Example 3

Ammonium fluoride (NH_4F), water and an organic solvent having a hetero atom were mixed at the ratios shown in Table 2. The mixtures were filtrated using a
5 filter paper to remove crystals therefrom, giving etching solutions. The etch rate and selectivity of the etching solutions were determined using two test substrates: one comprising a silicon substrate and a THOX film formed thereon, the other comprising a silicon substrate and a
10 BPSG film formed thereon. The results are shown in Table 2.

[0033]

Table 2

Ammonium fluoride/organic solvent/water etching solution

Ex.	Organic solvent	Relative dielectric constant	NH ₄ F concentration (%)	Organic solvent concentration (%)	Water concentration (%)	THOX etch rate (Å/min.)	BPSG etch rate (Å/min.)	Selectivity
Ex. 4	Acetic acid	6.2	1.85	98.15	0	77	70	0.91
Ex. 5	IPA	19.9	1.48	93.52	5.0	8	10	1.25
Ex. 6	Ethanol	24.6	1.48	93.52	5.0	11	15	1.36
Ex. 7	Ethanol	32.7	1.47	97.02	1.5	8	11	1.38
Comp. Ex. 3	(Water)	78.3	1.48	0	98.52	<3	<3	--

Example 8 and Comparative Examples 4-7

Ammonium monohydrogendifluoride ($\text{NH}_4\text{F} \cdot \text{HF}$), ammonium fluoride (NH_4F), water and an organic solvent having a hetero atom were mixed at the ratios shown in Table 3. The mixtures were filtrated using a filter paper to remove crystals therefrom, giving etching solutions. The etch rate and selectivity of the etching solutions were determined using two test substrates: one comprising a silicon substrate and a THOX film formed thereon, the other comprising a silicon substrate and a BPSG film formed thereon. The results are shown in Table 3.

[0034]

Table 3
Ammonium monohydrogenbifluoride/ammonium fluoride/organic solvent/water

etching solution

	Organic solvent	Relative dielectric constant	NH ₄ F·HF concentration (%)	NH ₄ F concentration (%)	Organic solvent concentration (%)	Water concentration (%)	THOX etch rate (Å/min.)	BPSG etch rate (Å/min.)	Selectivity
Ex. 8	Ethanol	24.6	0.7125	1.48	92.81	5.0	28	35	1.25
Comp. Ex. 4	(Water)	78.3	0.7125	9.5375	0	89.75	59	163	2.76
Comp. Ex. 5	(Water)	78.3	0.7125	19.5375	0	79.75	63	153	2.43
Comp. Ex. 6	(Water)	78.3	0.7125	29.5375	0	69.75	59	107	1.81
Comp. Ex. 7	(Water)	78.3	0.7125	39.5375	0	59.75	43	66	1.53

Examples 9-13 and Comparative Example 8

Ammonium monohydrogenbifluoride ($\text{NH}_4\text{F}\cdot\text{HF}$),
water and IPA were mixed at the ratios shown in Table 4.
The mixtures were filtrated using a filter paper to
5 remove crystals therefrom, giving etching solutions. The
etch rate and selectivity of the etching solutions were
determined using two test substrates: one comprising a
silicon substrate and a THOX film formed thereon, the
other comprising a silicon substrate and a BPSG film
10 formed thereon. The results are shown in Table 4.

[0035]

Table 4
Ammonium monohydrogenbifluoride/2-propanol/organic solvent/water etching solution

Ex.	Organic solvent	Relative dielectric constant	NH ₄ F·HF concentration (%)	Organic solvent concentration (%)	Water concentration (%)	THOX etch rate (Å/min.)	BPSG etch rate (Å/min.)	Selectivity
Ex. 9	IPA	19.9	0.1425	98.8575	1.0	19	18	0.95
Ex. 10	IPA	19.9	0.1425	98.3575	1.5	12	13	1.08
Ex. 11	IPA	19.9	0.1425	97.8575	2.0	17	23	1.35
Ex. 12	IPA	19.9	0.1425	97.3575	2.5	24	33	1.38
Ex. 13	IPA	19.9	0.1425	96.8575	3.0	24	36	1.50
Comp. Ex. 8	IPA	19.9	0.1425	94.3575	5.0	23	43	1.87

Examples 14-15 and Comparative Examples 9-10
Ammonium fluoride (NH_4F), water and ethanol
were mixed at the ratios shown in Table 5. The mixtures
were filtrated using a filter paper to remove crystals
5 therefrom, giving etching solutions. The etch rate and
selectivity of the etching solutions were determined
using two test substrates: one comprising a silicon
substrate and a THOX film formed thereon, the other
comprising a silicon substrate and a BPSG film formed
10 thereon. The results are shown in Table 5.

[0036]

Table 5
Ammonium fluoride/ethanol/water etching solution

	Organic solvent	Relative dielectric constant	NH ₄ F concentration (%)	Organic solvent concentration (%)	Water concentration (%)	THOX etch rate (Å/min.)	BPSG etch rate (Å/min.)	Selectivity
Ex. 14	Ethanol	24.6	1.48	97.02	1.5	8	10	1.25
Ex. 15	Ethanol	24.6	1.48	88.52	10.0	13	18	1.38
Comp. Ex. 9	Ethanol	24.6	1.48	83.52	15.0	12	29	2.42
Comp. Ex. 10	Ethanol	24.6	1.48	68.52	30.0	<3	27	--

Examples 16-19 and Comparative Examples 11-12

Ammonium fluoride (NH_4F), water and acetic acid were mixed at the ratios shown in Table 6. The mixtures were filtrated using a filter paper to remove crystals therefrom, giving etching solutions. The etch rate and selectivity of the etching solutions were determined using two test substrates: one comprising a silicon substrate and a THOX film formed thereon, the other comprising a silicon substrate and a BPSG film formed thereon. The results are shown in Table 6.

[0037]

Table 6
Ammonium fluoride/acetic acid/water etching solution

Ex.	Organic solvent	Relative dielectric constant	NH ₄ F concentration (%)	Organic solvent concentration (%)	Water concentration (%)	THOX etch rate (Å/min.)	BPSG etch rate (Å/min.)	Selectivity
Ex. 16	Acetic acid	6.2	0.2775	99.7225	0	27	38	1.41
Ex. 17	Acetic acid	6.2	0.37	99.63	0	72	67	0.93
Ex. 18	Acetic acid	6.2	0.37	96.3	1.0	73	95	1.31
Ex. 19	Acetic acid	6.2	0.925	99.075	0	73	69	0.95
Comp. Ex. 11	Acetic acid	6.2	3.7	96.3	0	104	101	0.97
Comp. Ex. 12	Acetic acid	6.2	0.37	96.3	3.0	75	154	2.05

Example 20 and Comparative Examples 13-14

Ammonium monohydrogenbifluoride ($\text{NH}_4\text{F} \cdot \text{HF}$), water and an organic solvent having a hetero atom were mixed at the ratios shown in Table 7.

5 The mixtures were filtrated using a filter paper to remove crystals therefrom, giving etching solutions. The etch rate and selectivity of the etching solutions were determined using test substrates each
10 comprising a silicon substrate and one of undoped oxide films (THOX, TEOS) and doped oxide films (BSG, BPSG, PSG, AsSG) formed thereon. The results are shown in Table 7.

[0038]

Table 7

Etch rates of doped films and undoped films

	Ex. 20	Comp. Ex. 13	Comp. Ex. 14
Organic solvent	IPA	(Water)	(Water)
Relative dielectric constant	19.9	78.3	78.3
NH ₄ F·HF concentration (%)	0.57	0.57	0.7125
NH ₄ F concentration (%)	0	0	39.5375
Organic solvent concentration (%)	98.675	0	0
Water concentration (%)	0.755	99.43	59.75
Etch rate			
THOX etch rate (Å/min.)	38	22	43
TEOS etch rate (Å/min.)	47	39	61
BSG etch rate (Å/min.)	48	171	93
BPSG etch rate (Å/min.)	39	179	66
PSG etch rate (Å/min.)	43	63	75
AsSG etch rate (Å/min.)	40	174	120
Etch rate selectivity			
TEOS/THOX	1.24	1.77	1.42
BSG/THOX	1.26	7.77	2.16
BPSG/THOX	1.03	8.14	1.53
PSG/THOX	1.13	2.86	1.74
AsSG/THOX	1.05	7.91	2.79

[Document Name] Abstract

[Abstract]

[Object]

5 An object of the present invention is to provide a
composition for etching doped and undoped oxide films at
the same rate.

[Method for Achieving the Object]

10 An etching solution having a thermal oxide (THOX)
film etch rate and a boron phosphosilicate glass (BPSG)
film etch rate at 25°C of 100Å/min or lower and the ratio
of (BPSG etch rate) / (THOX etch rate) of 1.5 or lower.

[Selected Figure] Not present